

TiO₂ paste for DSSC photoanode: preparation and optimization of application method

I. O. Selyanin^{ab*}, A. S. Steparuk^c, R. A. Irgashev^{bc},
 A. V. Mekhaev^c, G. L. Rusinov^{bc}, A. S. Vorokh^{ab}

^a Institute of Solid State Chemistry,
 Ural Branch of the Russian Academy of Sciences,
 91 Pervomaiskaya St., Ekaterinburg 620990, Russia

^b Ural Federal University,
 19 Mira St., 620002, Ekaterinburg, Russia

^c Postovsky Institute of Organic Synthesis,
 Ural Branch of the Russian Academy of Sciences,
 S. Kovalevskoi/Akademicheskaya 22/20 St., 620137, Ekaterinburg, Russia
 *email: theselyanin@yandex.ru

Abstract. We propose a simple method of TiO₂ paste preparation from titania powder (Degussa) and organic binders (terpineol, ethyl cellulose) for making a continuous photoactive layer of a dye-sensitized solar cell (DSSC). The prepared paste was characterized by using thermogravimetric and X-ray diffraction methods for comparison with commercial paste (Solaronix). The TiO₂ layer parameters for applying and annealing were optimized by varying the layer thickness and using different masks. The surface morphology of annealed layers was controlled by optical microscopy. Before TiO₂ paste applying and after annealing, the conductive glass (fluorine-tin oxide — FTO) was treated by TiCl₄ hydrochloric acid solution. The structure of DSSCs were composed FTO-glass / TiO₂ layer sensitized Ruthenium complex (**N719** dye)/ iodide-based electrolyte / Pt counter electrode/ FTO glass. The DSSC photovoltaic characteristics were measured under AM 1.5G irradiation and demonstrated to be close to those of photoanodes based on the prepared and commercial pastes.

Keywords: DSSC; Gratzel cell; TiO₂ paste; photoanode; open-circuit photovoltage; short-circuit photocurrent density; I–V characteristics

Received: 27.03.2020. Accepted: 20.10.2020. Published:30.12.2020.

© Selyanin I. O., Steparuk A. S., Irgashev R. A., Mekhaev A. V., Rusinov G. L., Vorokh A. S.,
 2020

Introduction

Over the past two decades, DSSCs (dye-sensitized solar cells or Gratzel cells) have become widely known due to their environmental friendliness and low cost of manufacture [1]. Improving the efficiency of the solar irradiation conversion into electrical energy can be reached by modifying every individual cell

element. A photoactive anode layer based on wide-band semiconductor oxides (usually, nanocrystalline TiO₂) plays the most important role [2, 3]. Titania matrix can be sensitized by organic molecules or quantum dots to allow the efficient injection of light-excited electrons from dyes [4]. The combination of TiO₂ phases (anatase,

rutile, brookite, and amorphous) improves the conducting and catalytic properties of anode material. For commercial and laboratory investigation of photoanode, a crystalline phase of anatase or a mixture of anatase and rutile phases (for example, Degussa P25 with the ratio of anatase: rutile = 3:1) are used as sources of TiO_2 for paste making [5, 6].

Together with the TiO_2 phase composition and electronic structure, the layer's geometrical and morphological characteristics play an important role in electricity generation. In particular, the photoanode TiO_2 layer thickness affects the photovoltaic cell characteristics directly: the thick oxide layer is prone to cracking after shrinkage [6]. The cracks impede the electron transfer, provoke the short circuit, and reduce the area of the photoactive surface. A balance between oxide layer continuity and thickness should be found to optimize the DSSC operation. When TiO_2 nanocrystalline layer thickness increases from 0.5 to 2 μm , the solar cell characteristics behave as follows: the short-circuit current density increases by a third, and the open-circuit voltage increases by 5% [7]. The dependence of photoelectrochemical characteristics on TiO_2 layer thickness (6, 10, 14 μm) demonstrates that the opti-

mal layer thickness is 10 μm for good light absorption, minimal charge recombination, and the low resistance to charge transfer [8]. The short-circuit current and conversion efficiency decrease when the TiO_2 layer thickness exceeds 15 μm [9–12]. The good anode layer continuity and its certain thickness are necessary to obtain the high efficiency of DSSC.

The purpose of this work is to develop methods for producing a paste based on TiO_2 powder and forming a continuous layer of optimal thickness on a conductive substrate. The phase and chemical composition of commercial and prepared pastes were studied by X-ray diffraction and thermogravimetric analysis. The search for optimal parameters of heat treatment and formation of the layer of a given thickness was carried out by studying the behavior (preservation of continuity or cracking) of commercial paste on laboratory glass. The obtained parameters were used to create DSSC anodes, the photoactive layers of which are formed from both commercial and prepared pastes. A dye **N719** based on a ruthenium complex was adsorbed on the TiO_2 layer. The photovoltaic properties of the collected DSSC were studied under the conditions of illumination of AM 1.5G by a xenon light source.

Experimental

Paste preparation and characterization. For the paste preparation, 1.0 g of TiO_2 (Degussa P25, Sigma-Aldrich), 3.8 g of α -terpineol (70% PS, Panreac), 0.5 g of ethyl cellulose (48.0–49.5% (w/w) ethoxyl basis, Sigma-Aldrich), 0.15 g of nitric acid (65%, Vecton) in 20 ml of ethyl alcohol were mixed. The mixture was stirred for 30 minutes at room temperature. The titania-containing paste was obtained by distilling excess volatile components

on a Heidolph Hey-VAP Precision rotary evaporator at a water bath temperature of 60 °C and reduced pressure (175 mbar) for 30 minutes. Commercial paste Ti-Nanoxide D/SP (Solaronix SA) was used as a reference for comparison of viscosity and homogeneity. The standard doctor blade method was used for applying pastes in all cases. The area of the applied layer was 2.0×2.0 cm.

The morphology of samples with pastes was studied using a Carl Zeiss Neophot 30 optical microscope equipped with a digital camera EverFocus EQ500A/P-IR. X-ray diffraction (XRD) studies were performed on the Shimadzu MAXima-X XRD-7000 X-ray diffractometer (with Cu K α radiation, $\lambda=1.5406$ Å) in the geometry of Bragg-Brentano with a step of 0.03° at the angle of 2θ and an exposure time of 3 seconds. Particle size was determined by the Igor Pro Multipeak2 program using the Scherrer formula $D = K\lambda/(\text{FWHM}\cdot\cos\theta)$, where K is the form factor, λ is the X-ray wavelength, FWHM is full width at half maximum and θ is the Bragg angle corresponding to reflection. Thermogravimetric studies of commercial and prepared pastes based on titanium dioxide were performed on a Mettler Toledo TGA / DSC 1 device in the air (30 ml/min) with a heating rate of $10^\circ\text{C}/\text{min}$ in the range of $30\text{--}500^\circ\text{C}$.

Optimization of annealing and paste application. Glass substrates were kept in a sulfochromic mixture for 24 hours, afterward rinsed with distilled water and isopropyl alcohol and dried at 100°C . To regulate the thickness of the paste layer, masks made of various materials were used, namely: adhesive tape (hereinafter — a.t., $35\text{ }\mu\text{m}$), aluminum foil (9 and $14\text{ }\mu\text{m}$), screen printing mesh Sefar E-MESH 61/156-64W PW (thread thickness $64\text{ }\mu\text{m}$, cell size $100\times 100\text{ }\mu\text{m}$). The paste application onto the cover glass was made using a doctor blade technique. Samples with the paste were dried at 120°C for 5 minutes, then annealed in a muffle furnace (SNOL with OVEN TRM-10 regulator) in the air at temperatures from 350 to 450°C for 30 minutes (the heating rate was $5^\circ\text{C}/\text{min}$). The study of the effect of 0.30 g nitric and perchloric acids

on the continuity of the formed layer was carried out by adding HNO_3 (65%, Vecton, $>90\%$ Sigma-Aldrich) or HClO_4 (65%, Vecton) to the commercial paste.

The formation of photoanodes. FTO (fluorine-doped tin oxide) conductive glasses (size $2.5\times 2.5\text{ cm}$, surface resistivity $\sim 8\text{ }\Omega/\text{cm}^2$, Sigma-Aldrich) were treated with isopropyl alcohol for 30 minutes and then dried at 50°C . Then FTO glasses were treated by holding in the TiCl_4 hydrochloric acid solution ($\geq 98.0\%$, Fluka) for 30 minutes at a solution temperature of 70°C , followed by washing with isopropyl alcohol and distilled water. After applying the oxide paste, the samples were annealed in a muffle furnace for 30 minutes at 450°C . The resulting layer was re-treated by holding in TiCl_4 hydrochloric acid solution according to the method described above. Adsorption of the dye N719 [di-tetrabutylammonium *cis*-bis(isothiocyanato)-bis(2,2-bipyridyl-4,4-dicarboxylate)ruthenium(II)] (Solaronix SA) onto the TiO_2 layer was carried out by holding the layer in a $5\cdot 10^{-4}$ M methanol solution of N719 for 18 hours.

The cell elements and assembly. To create a counter electrode, a thin layer of platinum was applied to the FTO glass using the following method: a few drops of H_2PtCl_6 solution in ethanol were distributed over the surface and annealed at 450°C for 30 minutes. A mixture of 0.5 M LiI (99%, Sigma-Aldrich) + 0.05 M I_2 (sublimated for analysis, Sigma-Aldrich) in acetonitrile (99.9%, NPO Reaktivy OSC) or 3-methoxypropionitrile ($\geq 98.0\%$, Sigma-Aldrich) was used as the electrolyte. The assembly of the elements was performed as follows: the Pt cathode was placed on top of the photoanode side soaked TiO_2 layer, then a few drops of electrolyte were added in the gap

between the two glasses, and then the glasses were stuck together using office clips.

Measurement of I–V characteristics. The assembled cell was illuminated with a xenon source Zolix Gloria-X500A (the illumination power at a distance of 25 cm is 100 mW/cm², determined using a silicon calibration element Zolix QE-B1). The source radiation spectrum was in the 250–1000 nm band with

the maximum intensity in the range of 350 to 550 nm. The illuminated surface of the photoanode was 4 cm². Lightening was performed from the photoanode side with the adsorbed dye. The I–V characteristic was recorded using a Keithley 2450 source-meter with a 50 mV step with a measurement error of ± 10 nA for current and ± 1 μ V for voltage.

Results and discussion

The prepared paste characterization and comparison with the commercial analog. The paste was made of TiO₂ Degussa P25 with the addition of α -terpineol, ethyl cellulose, and nitric acid (hereinafter “Prepared”). Three stages are distinguished on thermogravimetric curves (Fig. 1): the evaporation of volatile components (1st stage), oxidation of α -terpineol (2nd stage, $T_{b.p.} = 215$ °C), and the combustion of cellulose derivatives (3rd stage, $T_{autoignit.} = 370$ °C). After annealing, with the organic components removed, the remaining weight (pure TiO₂) was found to be $\sim 15\%$ of the initial one. The result obtained for the laboratory paste is comparable to the commercial paste Ti-Nanoxide D/SP (Solaronix SA).

The samples annealed at temperatures of 350–400 °C have a brownish tinge associated with incomplete burning of organic components. This result is consistent with the TGA data. Based on the obtained data, a temperature of 450 °C was used for further research. It is evident from Table 1 that annealing leads to cracking of the resulting layer, which can be avoided by varying the thickness of the applied layer.

According to XRD, the composition of the obtained layers at 450 °C is nanocrystalline TiO₂ powder (Fig. 2). The combustion of organic components is proved by the absence of any reflections or amorphous halo onto the diffrac-

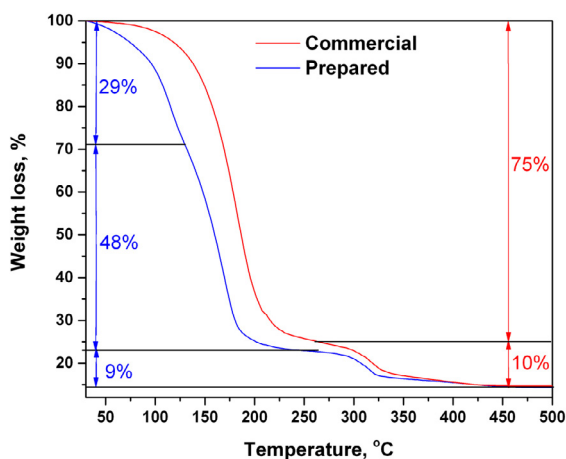
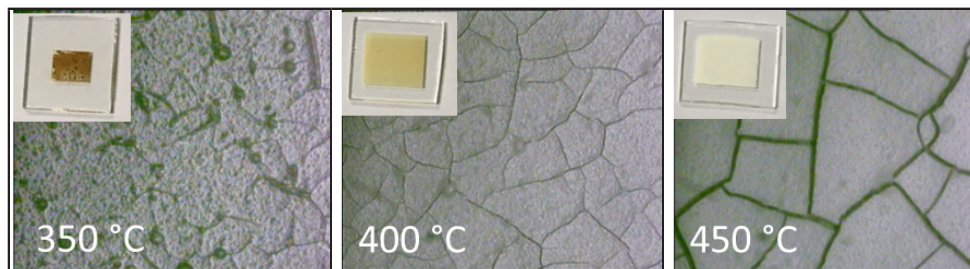


Fig. 1. Thermogravimetric curves of prepared and commercial pastes

Microphotographs of the TiO_2 layer surface,
the insets show layer surfaces on the glass substrate



tion pattern. The powder obtained from the annealed commercial paste consists of anatase nanoparticles with an average particle size of 20.7 nm. The prepared paste is based on TiO_2 -P25 and consists of a mixture of anatase (92 mass %) and rutile (8 mass %) phases. The size of anatase particles in TiO_2 -P25 was 19.8 nm, and the size of rutile particles was 27.9 nm.

We proposed that titania nanoparticles can be ordered along chains of organic molecules (ethyl cellulose) and can form anisotropic agglomerates during heat treatment. This process can provoke the texturizing of the TiO_2 layer. In support of this proposition, annealing was performed directly on the glass substrate used in the XRD experi-

ment. The peak intensities of both layer and powder are the same as the standard peak intensities defined by PDF cards (21–1272 for anatase, and 21–1276 for rutile). The difference curve between the layer and powder diffraction patterns shows a lack of crystallographic orientations of the layer. We can conclude that the procedure of heat treatment allows decomposing organic compounds and obtaining the titania layer with a random orientation of nanostructured grains. An amorphous halo occurs for both the prepared powder pattern and the difference curve because of the very thin oxide layer and the reflection from the glass substrate.

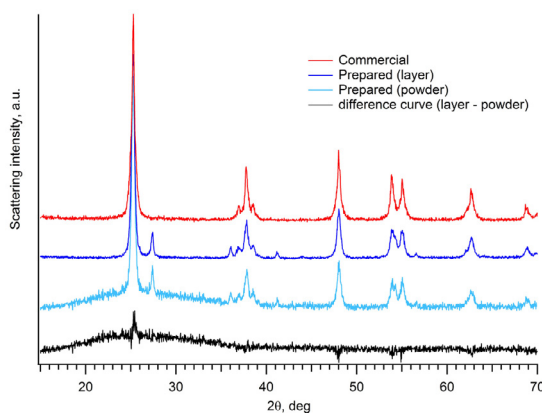


Fig. 2. Diffraction patterns of commercial and prepared TiO_2 layers and initial TiO_2 powder

Effect of various masks on the thickness of the TiO_2 layer. The commercial paste was used as a reference for searching the optimal method of applying the paste to form a continuous TiO_2 layer. This paste has a uniform small particle size and a verified ratio between the components of the paste: TiO_2 , thickener, and binder. To vary the thickness of the resulting layer on glass substrates, various combinations of a.t., aluminum foil of different thicknesses, and Sefar screen printing mesh were used. A.t. and foil were used as masks that were applied to the glass. The squeegee was used to apply the paste evenly. The screen mesh was applied on top of a glass or a mask, a layer was applied on top of a mask, and then the mesh was removed. The samples were exposed to temperature treatment corresponding to the “annealing” stage discussed in the previous section. Various “mask-mesh” combinations for applying TiO_2 paste to glass substrates and corresponding microscopic images of samples are shown in Table 2 (sections I–III).

Analysis of microphotographs of the obtained layers showed that the best results are obtained when using one layer of a.t. in the case of using the only a.t. It corresponds to the thickness of the applied paste of $\sim 35 \mu\text{m}$. In this case, the layer remains continuous; almost no cracks emerge (Table 2, section I). A comparative study by optical microscopy showed that the layer thickness after annealing was $\sim 10 \mu\text{m}$. The experiment with using more than one layer of the adhesive tape showed that the increase in the layer's thickness results in intense cracking of the TiO_2 layer after annealing. It negatively affects the efficiency of the cell. Foil without mesh does not allow getting a layer of appropriate quality, the combination of foil and mesh produces an effect similar to the combina-

tion of mesh and a.t. (Table 2, section II). Besides, the foil deforms easily when it overlays the glass. This suggests that the use of a foil mask is problematic. Applying two layers of paste with intermediate drying, in contrast, demonstrates good continuity (Table 2, section III).

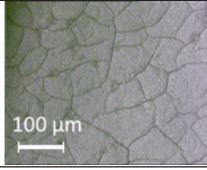


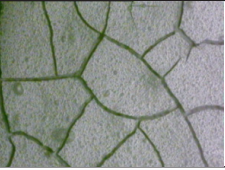
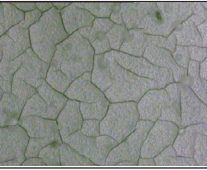
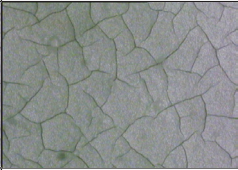
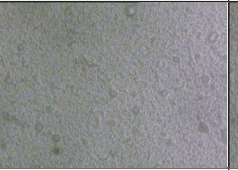
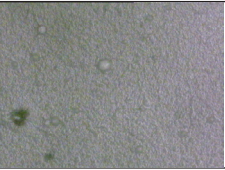


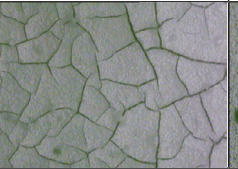
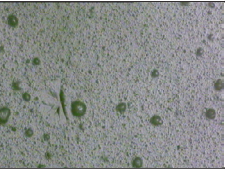

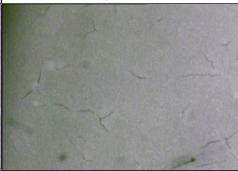
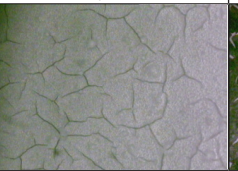
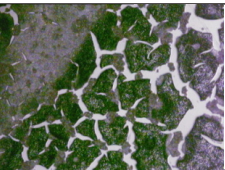
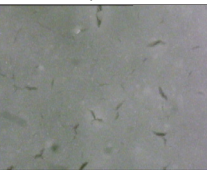
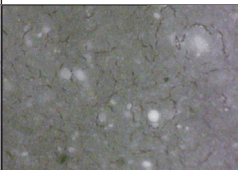

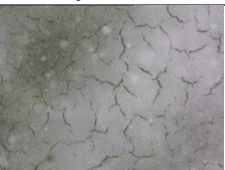
To test the hypothesis that cracking is primarily caused by uneven evaporation of the liquid phase and the formation of bubbles, an experiment with the addition of an oxidizer to a commercial paste to accelerate the oxidation process of organic components was performed. HNO_3 and HClO_4 acids were used as oxidants. Based on microphotographs of photoanode surfaces, it can be concluded that the layers have the best appearance after adding 65% HNO_3 , and adding HClO_4 , on the contrary, leads to greater cracking of the photoanode layer (Table 2-IV). In general, adding 65% and 90% HNO_3 oxidizer reduces the cracking of the oxide layer.

Having established the optimal mode of application, the samples were obtained with the prepared paste with combinations of masks presented in Table 2-V. From the presented images it is clear that the laboratory paste during the application has good continuity.

The fabrication of the photoanodes and the assembly of Gratzel cells. Based on the above experiments, the application and annealing conditions were selected for the preparation of photoanodes. In all cases, the commercial and the prepared pastes were applied through a mesh to a conductive FTO glass. To improve the continuity of the layer, preliminary (before applying the paste to the glass) and final (after applying and annealing the paste) treatments with TiCl_4 hydrochloric acid solution were performed.

Table 2

Micrographs of the surface of TiO_2 layers under various conditions for applying commercial paste (I–III) and its modification (IV), as well as methods for applying laboratory paste (V). The annealing temperature is 450 °C, the scale is shown on the upper-left microphotograph

I	1 layer a.t.	2 layer a.t.	3 layer a.t.	4 layer a.t.
				
II	9 μm foil	14 μm foil	9 μm foil– mesh	14 μm foil — mesh
				
III	mesh	1 layer a.t. — mesh	2 layer a.t. — mesh	1+1 layer a.t. — mesh*
				
IV	without oxidizer	HNO_3 (~65%)	HNO_3 (~90%)	HClO_4
				
V	1 layer a.t.	mesh	1 layer a.t. — mesh	TiCl_4 treatment
				
*	1 layer of a.t. — mesh, then drying at ~120 °C for 5 minutes, adding the 2 nd layer of a.t., applying the 2 nd layer of paste through the grid, followed by drying			

Strong adhesion of oxide layers plays an important role when they have been immersed in a dye solution for a long time. In the presence of microcracks and poor adhesion, even in the presence of distilled water, it is possible to observe the peeling of the oxide layer. For this reason, an additional experiment was performed to test

the adhesion properties. The prepared photoanode was immersed in distilled water for 24 hours, after which there was no delamination, the layer showed good resistance even under the mechanical influence.

According to optical microscopy data, the morphological differences between the layers of commercial and the prepared

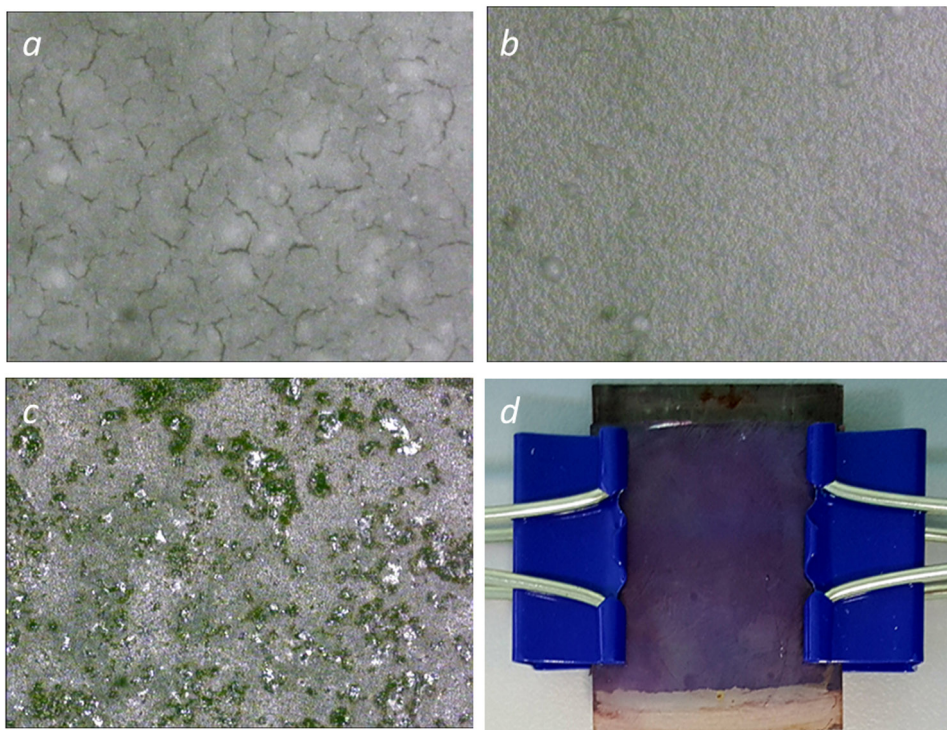


Fig. 3. Microscopic images of surfaces: photoanodes based on (a) prepared and (b) commercial pastes, (c) a cathode coated with a layer of Pt, (d) a cell assembled from the resulting electrodes

pastes are minor in comparison with other layers shown in Table 2. Both layers have good continuity, but in the case of prepared paste (Fig. 3a) there are cracks and slight heterogeneity caused by the aggregation of TiO_2 nanoparticles in the initial powder, while for commercial paste, small bubbles can be observed (Fig. 3b). A Pt thin layer applied to the conductive glass was used as a counter electrode (Fig. 3c). The surface of the assembled cell is shown in Fig. 3d.

Fig. 4 shows the I–V characteristics of the DSSCs. The value of the open-circuit photovoltage V_{oc} for the cell with prepared paste was 0.33 V, for the commercial paste V_{oc} was slightly higher — 0.38 V. At the same time, the short-circuit current density I_{sc} for the cell with prepared paste was 0.96 mA/cm^2 , which is noticeably

higher than for the element based on commercial paste — 0.6 mA/cm^2 .

To prevent the evaporation of acetonitrile from the electrolyte, the solvent was replaced with 3-methoxypropionitrile with a higher boiling point. The change of the electrolyte led to an increase in V_{oc} for both the cell with prepared paste — 0.5 V, and for the cell with commercial paste — 0.47 V. The I_{sc} values for the cell with prepared paste decreased to 0.9 mA/cm^2 , while for the cell with commercial paste, on the contrary, increased to 0.68 mA/cm^2 .

According to the data obtained, we conclude that I–V characteristics of DSSCs based on the prepared paste are close to the characteristics of DSSCs based on the commercial paste under the same conditions, namely: counter electrode, electrolyte, and assembly method. Replacing

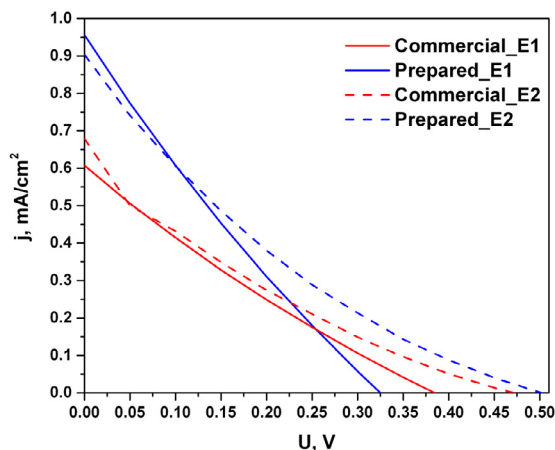


Fig. 4. I–V characteristics of assembled solar cells with various electrolytes: E1 — acetonitrile, E2–3-methoxypropionitrile

the solvent in the electrolyte increases both

the current values and the voltage between the cell electrodes.

Conclusions

To produce a homogeneous paste of nanodisperse TiO_2 , a combination of α -terpineol and ethyl cellulose as binding components was used. Applying the prepared paste to the pretreated glasses using a screen printing mesh and annealing at a temperature of 450°C allows forming a continuous layer of TiO_2 on the glass substrate.

The DSSCs assembled from the prepared and the commercial pastes demonstrated comparable photovoltaic charac-

teristics of photoanodes. The open-circuit photovoltage value reaches $0.4\text{--}0.5\text{ V}$; the short-circuit current density reaches 1 mA/cm^2 . The TiO_2 layers produced by using either prepared or commercial paste have similar properties, but the prepared paste is less expensive to manufacture. By changing other components (electrolyte, a counter electrode, etc.) and improving the assembly method, higher efficiency of DSSC can be achieved.

Acknowledgements

The team of authors is grateful to the Russian Science Foundation for financial support, grant No. 17-79-20165. A. S. Steparuk would like to acknowledge the financial support for the analytical studies of synthesized compounds from the Ministry of Education and Science of the Russian Federation within the framework of the State Assignment for Research (project no. AAAA-A19-119012490006-1).

References

1. Gratzel M. Mesoporous oxide junctions and nanostructured solar cells. *Curr. Opin. Colloid Interface Sci.* 1999;4(4):314–21. doi:10.1016/S1359-0294(99)90013-4

2. Joshi PH, Korfiatis DP, Potamianou SF, Thoma K-AT. Selected parameters leading to an optimized DSSC performance. *Russ. J. Electrochem.* 2013;49(7):628–32. doi:10.1134/S1023193513070045
3. Amit K, Sharma R, Pransu G, Boxman RL. Evaluation of the photo electrode degradation in dye sensitized solar cells. *Russ. J. Electrochem.* 2019;55(9):829–40. doi:10.1134/S1023193519090039
4. O'Regan B, Grätzel M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature.* 1991;353(6346):737–40. doi:10.1038/353737a0
5. Nizard H, Meyer T, Oberpriller H, Meyer M, Benien H. Assessment of photocatalytic activity of SolaronixTM nanostructured anatase, *Journal of Photochemistry and Photobiology A: Chemistry.* 2008;195(1):99–104. doi:10.1016/j.jphotochem.2007.09.012
6. Khalid Hossain M, Rahman MT, Basher MK. Influence of thickness variation of gamma-irradiated DSSC photoanodic TiO₂ film on structural, morphological and optical properties. *Optik.* 2019;178:449–60. doi:10.1016/j.ijleo.2018.09.170
7. Kao MC, Chen HZ, Young SL, Kung CY, Lin CC. The effects of the thickness of TiO₂ films on the performance of dye-sensitized solar cells. *Thin Solid Films.* 2009;517(17):5096–9. doi:10.1016/j.tsf.2009.03.102
8. Baglio V, Girolamo M, Antonucci V. Influence of TiO₂ Film Thickness on the Electrochemical Behaviour of Dye-Sensitized Solar Cells. *Int. J. Electrochem. Sci.* 2011;6:3375–84
9. Kumari JMKW, Sanjeevadarshini N, Dissanayake MAKL, Senadeera GKR, Thotawatthage CA. The effect of TiO₂ photo anode film thickness on photovoltaic properties of dye-sensitized solar cells. *Ceylon J. Sci.* 2016;45(1):33–41. doi:10.4038/cjs.v45i1.7362
10. Sedghi A, Miankushki HN. The Effect of Drying and Thickness of TiO₂ Electrodes on the Photovoltaic Performance of Dye-Sensitized Solar Cells. *Int. J. Electrochem. Sci.* 2015;10:3354–62
11. Fitra M, Daut I, Irwanto M, Gomes N, Irwan YM. Effect of TiO₂ Thickness Dye Solar Cell on Charge Generation. *Energy Procedia.* 2013;36:278–86. doi:10.1016/j.egypro.2013.07.032
12. Mathew A, Rao GM, Munichandraiah N. Effect of TiO₂ electrode thickness on photovoltaic properties of dye sensitized solar cell based on randomly oriented Titania nanotubes. *Mater. Chem. Phys.* 2011;127(1-2):95–101. doi:10.1016/j.matchemphys.2011.01.032